

COORDINATED IN SITU ANALYSES OF ORGANIC NANOGLOBULES IN THE SUTTER'S MILL

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Introduction: The Sutter's Mill meteorite is a newly fallen carbonaceous chondrite that was collected and curated quickly after its fall [1]. Preliminary petrographic and isotopic investigations suggest affinities to the CM2 carbonaceous chondrites. The primitive nature of this meteorite and its rapid recovery provide an opportunity to investigate primordial solar system organic matter in a unique new sample.

Organic matter in primitive meteorites and chondritic porous interplanetary dust particles (CP IDPs) is commonly enriched in D/H and ¹⁵N/¹⁴N relative to terrestrial values [2-4]. These anomalies are ascribed to the partial preservation of presolar cold molecular cloud material [2]. Some meteorites and IDPs contain μ m-size inclusions with extreme H and N isotopic anomalies [3-5], possibly due to preserved primordial organic grains.

The abundance and isotopic composition of C in Sutter's Mill were found to be similar to the Tagish Lake meteorite [6]. In the Tagish Lake meteorite, the principle carriers of large H and N isotopic anomalies are sub- μ m hollow organic spherules known as organic nanoglobules [7]. Organic nanoglobules are commonly distributed among primitive meteorites [8, 9] and cometary samples [10].

Here we report *in-situ* analyses of organic nanoglobules in the Sutter's Mill meteorite using UV fluorescence imaging, Fourier-transform infrared spectroscopy (FTIR), scanning transmission electron microscopy (STEM), NanoSIMS, and ultrafast two-step laser mass spectrometry (*ultra*-L²MS).

Samples & Methods: Comminuted matrix fragments (10-100 μ m) from Sutter's Mill meteorite #8 (SM#8 [5] after rain collection [11]) were selected for analyses and pressed onto KBr for initial FTIR characterization. Several fragments from the same batch were embedded in elemental S for ultramicrotomy and sliced into 70 nm sections that were deposited onto C-coated TEM grids for STEM-NanoSIMS coordinated analysis.

The primary mineralogy and distribution of carbonaceous phases of the microtomed thin sections were investigated using a JEOL 2500SE 200kV field-emission STEM equipped with a Noran thin window energy-dispersive X-ray (EDX) spectrometer, and a Gatan Tridiem imaging filter (GIF) for energy-filtered imaging (EFTEM) and EELS.

Carbon, N, and O isotopic images of microtome sections were acquired with the JSC NanoSIMS 50L in

multidetector with electron multipliers. Images were obtained by rastering a 0.5 pA, <100 nm Cs⁺ beam over a 10 μ m field of view and were repeatedly acquired to obtain a total of 30 – 50 image layers for each analysis. The duration of each analysis ranged from 2-3 hours. 10 μ m grains of NBS standard graphite and 1-hydroxy benzotriazole hydrate served as external isotopic standards for C and N, while O isotopes were internally normalized.

Matrix fragments were pressed into Au foil for *ultra*-L²MS analysis. Prior to *ultra*-L²MS measurements, native fluorescence images were acquired under 380 nm UV illumination. This has previously proved effective in non-destructively identifying organic nanoglobules within meteorite matrix.

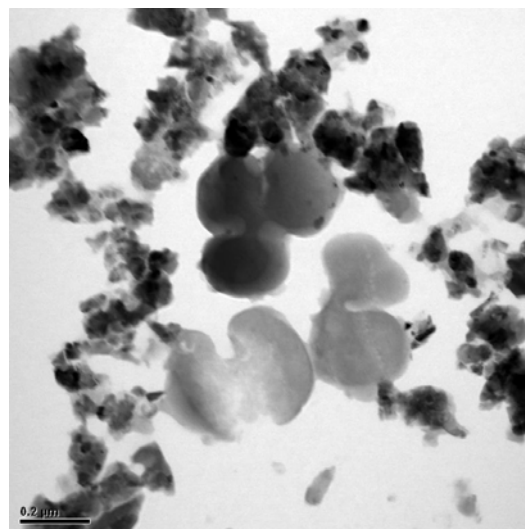


Fig. 1 Brightfield STEM image of an organic globule cluster. Scale bar shows 200 nm.

Results: FTIR In the FTIR studies, the matrix fragments from SM#8 we studied fell to three distinct lithology groups: 1) Dominated by olivine, carbonate and minor phyllosilicates associated with minor aliphatic hydrocarbons 2) Carbonate and phyllosilicate-free, olivine, pyroxene and amorphous silica mixture with trace aliphatic hydrocarbons, and 3) Dominated by phyllosilicates and carbonates, with minor olivine and abundant aliphatic hydrocarbons. The strength of the aliphatic features is positively correlated with the 3 μ m OH feature.

STEM: The SM#8 matrix grains we observed in STEM consist of fine-grained (<1 μ m) crystalline silicates of olivine, pyroxene, and diopside, and Ni-rich

metal and sulfides (pyrrhotite and pentlandite) set in an amorphous silicate matrix. The amorphous silicates contain Fe-sulfides and metal nanophase grains. The samples were free from carbonates and phyllosilicates which occur in lithology #2 in our FTIR measurement.

Two types of carbonaceous materials were observed in the samples: 1) non-shape filling material in the gaps between mineral grains and 2) hollow and filled globules. Fourteen nanoglobules were found among three thin sections surveyed. Some globules exhibit distinctive rims on their surfaces (Fig. 1). These initial observations suggest differing morphologies from the mostly hollow organic globules in Tagish Lake and vesicular textures in Bells [7, 8].

NanoSIMS: Each of the 14 globules identified in TEM observations yielded distinct ^{15}N -rich hotspots in isotopic images, with $\delta^{15}\text{N}$ values ranging from 290 – 630 ‰ (Fig. 2). In fact, the globules accounted for all of the N anomalous regions in the ion images, where the bulk $\delta^{15}\text{N}$ value was normal ($16 \pm 10\text{‰}$). In contrast, the C isotopic compositions of the globules were isotopically normal and indistinguishable from the matrix ($\delta^{13}\text{C} = -14 \pm 5\text{‰}$) within error. We did not identify any grains in these images having isotopically anomalous O.

UV Fluorescence & ultra-L²MS: In sharp contrast to other carbonaceous meteorites, nanoglobules in SM#8 showed no discernable native fluorescence. Subsequent organic spatial mapping by ultra-L2MS showed the abundance and compositional diversity of organics to be broadly similar to other CM-type meteorites. However, the spatial distribution showed a clear dichotomy of organic-rich and organic-poor regions on 10 to 100 μm spatial scales.

Discussion: As generally described in [1], the matrix fragments from SM#8 also show mineralogical heterogeneity at the sub- μm scale. Mineralogically, the SM#8 matrix fragments are mineralogically similar to Acfer 094 matrix, a unique and primitive ungrouped carbonaceous chondrite [12], although the crystalline silicates are not as Mn or Cr rich as those in Acfer 094.

The levels of ^{15}N -enrichment in the globules we measured are comparable to those previously measured in other primitive meteorites such as Bells and Tagish Lake, and those in cometary samples [7-10]. Their stark isotopic contrast from the surrounding matrix indicates that they formed prior to the host meteorite in a cold outer nebular or presolar environment. Yet the differing morphologies and isotopic compositions observed in organic globules in different meteorites appear to reflect the differing extent of later nebular or parent body processing. It is interesting to note that the globules studied here occurred in an anhydrous matrix,

in contrast to those previously studied in Bells and Tagish Lake.

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References: [1] Jenniskens P. et al. (2012) *Science* 338, 1583-1587. [2] Messenger S. & Walker R.M. in *Astro-physical Implications of the Laboratory Study of Presolar Materials* (1997), p.545. [3] Messenger S. (2000) *Nature* 404, 968. [4] Busemann H. et al. (2006), *Science* 312, 727. [5] Floss C. et al. (2004) *Science* 303, 1355. [6] Grady M. M. et al. (2012) *MAPS Suppl.* #5253. [7] Nakamura-Messenger K. et al. (2006) *Science*, 314, 1439. [8] Messenger S. et al. (2008) *LPSC* 39, #2391. [9] de Gregorio B. T. et al. (2010) *LPSC* 41, #2108. [10] Matrajt G. et al. (2012) *MAPS* 47, 525-549. [11] Jenniskens P. & Zolensky M. E. (2012) *Met. Bull.* 46, 1. [12] Keller L.P. et al. (2009) *MAPS Suppl.* #5371.

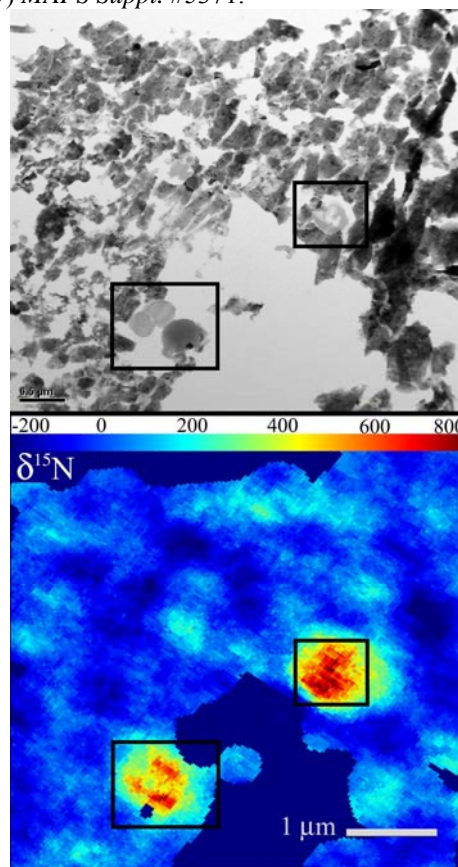


Fig. 2 Top: Bright field STEM image of section containing 4 organic globules. Bottom: N isotopic image showing two distinct ^{15}N -rich spots associated with the globules.